GAZ PHASE IR AND UV SPECTROSCOPY OF NEUTRAL CONTACT ION PAIRS

SANA HABKA, VALERIE BRENNER, MICHEL MONS, ERIC GLOAGUEN, *CEA Saclay, LIDYL, Gif-sur-Yvette, France*.

Cations and anions, in solution, tend to pair up forming ion pairs. They play a crucial role in many fundamental processes in ion-concentrated solutions and living organisms. Despite their importance and vast applications in physics, chemistry and biochemistry, they remain difficult to characterize namely because of the coexistence of several types of pairing in solution. However, an interesting alternative consists in applying highly selective gas phase spectroscopy which can offer new insights on these neutral ion pairs. Our study consists in characterizing contact ion pairs (CIPs) in isolated model systems (M^+, Ph-$(CH_2)_n$-COO^- with M=Li, Na, K, Rb, Cs, and n=1-3), to determine their spectral signatures and compare them to ion pairs in solution. We have used laser desorption to vaporize a solid tablet containing the desired salt. Structural information for each system was obtained by mass-selective, UV and IR laser spectroscopy combined with high level quantum chemistry calculations[1]. Evidence of the presence of neutral CIPs was found by scanning the π-π^* transition of the phenyl ring using resonant two-photon ionization (R2PI). Then, conformational selective IR/UV double resonance spectra were recorded in the $CO_2{}^-$ stretch region for each conformation detected. The good agreement between theoretical data obtained at the BSSE-corrected-fullCCSD(T)/dhf-TZVPP//B97-D3/dhf-TZVPP level and experimental IR spectra led us to assign the 3D structure for each ion pair formed. Spectral signatures of (M^+, Ph-CH_2-COO^-) pairs, were assigned to a bidentate CIPs between the alkali cation and the carboxylate group. In the case of (Li^+, Ph-$(CH_2)_3$-COO^-) pairs, the presence of a flexible side chain promotes a cation-π interaction leading to a tridentate O-O-π structure with its unique IR and UV signatures. IR spectra obtained on isolated CIPs were found very much alike the ones published on lithium and sodium acetate in solution[2]. However, in the case of sodium acetate, solution spectra were assigned to solvent shared pairs. Yet, the striking resemblance with our spectral data raises questions about the type assigned, pointing out that CIPs could be more present in these electrolyte solutions than previously thought. The novelty of the gas phase approach to investigate neutral ion pairs, opens the door for various new spectroscopic studies, paving the way to greater knowledge regarding the properties of ion pairs in many scientific fields. 1. Gloaguen, E.; Mons, M.; Topics in Current Chemistry, 2015, Vol 364, 225-270 2. Rudolph, W.W.; Fischer, D.; Irmer, G.; Dalton Transactions 2014, 43, (8), 3174-3185